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A Green Route Synthesis of Imines and Diimines from β-amino Alcohols as Promising Enantiopure Ligands.

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ABSTRACT

Although presence of water in organic synthesis is considered as contaminant and particularly disadvantageous for conventional imine synthesis, such synthesis is made possible in aqueous media without any catalyst in mild conditions. (R)-2-phenyl glycine, (S)-2-phenyl glycine, (R)-2-amino-3-phenylpropanoic acid and (S)-valine are easily reduced to their corresponding β-amino alcohols and are effectively condensed with various aromatic aldehydes and dialdehydes to obtain chiral imines and diimines (Schiff bases) in water as possible mixed (N,O) donor chiral ligands. The monoimines and diimines are well characterized and the specific rotations are measured in MeOH/CH_2Cl_2 at room temperature. UV-Vis. absorption spectroscopy studied for structural differences in the chiral Schiff' bases which signify strong intra molecular H-bonding in orthohydroxy Schiff bases and absorbs at longer wave lengths due to co planarity of the aromatic ring and azomethine chromophore.

Keywords: Chiral ligands, imines, diimines, aqueous medium, β-amino alcohols

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INTRODUCTION

In recent years water has emerged as a versatile solvent for organic synthesis. Water as a solvent in chemical manufacturing is not only inexpensive and environmentally benign, but also provides safety in operational processes and social benefits [1]. In early decades it was believed that, water is a contaminant in organic synthesis [2] but now days, extra-ordinary attention has been paid to organic reactions in water. Research and development in this area is still increasing exponentially [3]. Due to environmental concern it has become inevitable to develop a "Green" process of synthesis for bulk materials that avoids the use of potentially harmful or non renewable organic solvents [4]. Organic chemistry in water is not limited to classical organic transformations such as hydrolysis, esterification and substitutions but almost all organic reactions are explored in aqueous medium with more or less successful results [2, 3].

Asymmetric catalysis is growing rapidly, the industrial production of enantiomerically enriched compounds requires use of expensive chiral catalysts. The synthesis and purification of these chiral catalysts is tedious and laborious. Chiral imines or Chiral Schiff's base ligands (CSBLs) [5] are extensively used as chiral ligands in the synthesis of transition metal complexes as successful catalysts [6, 7]. Generally such imines are synthesized by simple condensation of aldehydes / carbonyl compounds with primary amines in anhydrous organic solvents[8]. The difficult task of elimination of water from reaction mixture is often achieved by addition of drying agents such as Na_2SO_4[9-11], $MgSO_4$[12-14], or by refluxing the reaction mixture in Dean-Stark apparatus [15, 16], for several hours and this method is still in practice to synthesize the diimines[17]. More recently CSBLs are synthesized by refluxing aldehydes or carbonyl compounds with primary amines in EtOH or MeOH[18-21]. This method consumes most of the time to obtain final product, since reaction mixture is refluxed for prolonged time and then kept for slow evaporation of solvent to get required imine, the chances of epimerization cannot be ruled out in such cases. CSBLs can form variety of transition metal complexes [22] by participating in binding with metal ions via nitrogen lone pair electrons. The chiral metal complexes of imine showed high enantioselectivity in organic transformation such as nitroaldol (Henry) reaction [18] and hydro phosphonylation of aldehydes[23]. Hence it has become primarily important to explore, simple, inexpensive, racemization free and environment friendly route to synthesize the CSBLs.

Our main aim is to synthesize the chiral metal complexes of imines, which could be used for the several asymmetric transformations in organic chemistry. To synthesize these complexes chiral imines are required in bulk quantities. Thus on scrutinizing the chemical literature we found that few aromatic Schiff bases were synthesized in saturated aqueous solutions and in the presence of various catalysts at different pH values [24]. A recent report [25] where imines, diimines and macrocyclic diimines are synthesized in aqueous solutions has prompted us to report our results in this field. Our final target was to prepare variety of chiral imines and diimines from optically active β-amino alcohols. Optically active α-amino acids *viz*. R-2-phenylglycine, (S)-2-phenylglycine, (R)-2-amino-3-phenylpropanoic acid and (S)-valine are conveniently reduced to their corresponding β-amino alcohols by using $NaBH_4$/ I_2 in dry THF according to minor modification in the known procedure[26] as a primary source of optically active compounds.

These β-amino alcohols on simple condensation with aromatic aldehydes in water under mild condition offered the imines and diimines in quantitative yields. All the reactions were carried out in the simplest manner, by mixing directly the β-amino alcohols and aromatic aldehydes in water, without adding any other organic solvent, catalyst or buffer solution at room temperature. When the imines did not separate directly from the aqueous solution, extraction was used. However, these unusual, but simple, economically practical reaction conditions are of wide application and of preparative value in the field of CSBLs synthesis. To the best of our knowledge there is only one report so far disclosed by László Lázár and co workers [27] where in condensation of (S)-2-amino-2-phenylethanol or (S)-2-amino-3-phenylpropanol with substituted benzaldehydes is carried out in methanol and water. The method is successful only for imines of aromatic aldehyde and aryl amines. Other reports for reactions in water [28, 29] are devoted to synthesis of non chiral Schiff bases. The synthesis of chiral imines in aqueous solutions for present work is reported in two sections: first, the general experiments which show the scope and limitations of the chiral imine synthesis in water and second the synthesis of open chain diimines that are promising chelating agents for metallic cations.

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MATERIALS AND METHODS

General details

Distilled water was used in all experiments. The optically active β-amino alcohols (**1-4**) were prepared by reduction of optically pure α-amino acids. Monoaldehydes (**5-8)** were purchased from local chemical companies and were purified before use. Dialdehydes (**9-12)** were synthesized by known procedure and purified by recrystallization before use. Some of these β-amino alcohols are commercially available.

All melting points recorded are uncorrected. NMR spectra were recorded on Varian Mercury Y. H., 300MHz spectrometer in $CDCl_3$ with $(Me)_4Si$ as internal standard and chemical shifts recorded in δ units. Coupling constants are given in Hz. Identification of monoimines were made by GC and comparing of mps with literature values were done where ever applicable. Infra red spectra were recorded on FT-IR 8400 Shimadzu model as KBr discs. The characteristics absorption is reported as broad (br), strong (s), medium (m) or weak (w) bands. Optical rotations were recorded on Perkin-Elmer polarimeter in a quartz cell of 1 dm at room temperature using sodium D-line and suitable solvent that is reported along with concentration in g/100ml. Elemental analysis was performed on Thermoflash microanalyzer with K factors calibration method.

General procedures for synthesis of monoimines: 1b-6b and 1c-8c.

In a standard procedure, in a round bottom flask equipped with Teflon coated magnetic bar with a magnetic stirrer and optionally with a reflux condenser were introduced 10 mmol of aldehydes and 25 ml distilled water. The β-amino alcohol (10mmol) was added in one portion and the flask was kept at room temperature under vigorous mechanical stirring for overnight in the case of monoimines **1b-6b** and 6-10 hours for **1c-8c.** Monoamines (**1c-8c**) were separated from aqueous medium within mixing time but stirring at room temperature continued till all starting aldehyde is converted into imine (TLC). If no precipitation occurred, the aqueous reaction mixture was extracted thrice with diethyl ether. The combined organic layers were dried over Na_2SO_4. The organic solvent was evaporated off and the residues were analyzed by GC and NMR. All the synthesized monoimines are fine solids and are purified by recrystallization from hot pet ether except for compounds (**5c** and **8c**) which were purified by column chromatography (Hexane: ethyl acetate, 80:20).

The experimental data for **1b-6b** and **1c-8c**

(R)-(+)-2-(4-methoxybenzylideneamino)-2-phenylethanol(**1b**)

Colourless floppy mass, mp 85^{0}C (Pet ether: ethyl acetate, 80:20), $[\alpha]_D^{27}$= 98.72^0 (c 1, MeOH), Yield (1.68g, 68%), IR(KBr), ν_{max}/cm^{-1} 3198, 1639, 1602, 1508, 1454, 1383, 1305, 1263, 1172, 1880, 1030, ^{1}H NMR ($CDCl_3$,300 MHz) δ = 8.32 (s,1H), 7.83 (d, 2H, J = 8.54Hz), 7.2-7.5 (m, 5H), 6.95 (d,2H, J = 8.54Hz), 4.91 (t, 1H, J = 4,27Hz), 3.87 (s. 3H), 2.45 (brs, 1H). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49; O, 12.53. Found: C, 74.97, H, 6.71, N, 5.61.

(S)-(-)-2-(4-methoxybenzylideneamino)-2-phenylethanol **(2b)**

Fine needles, mp 94-95^{0}C (Pet ether: ethyl acetate, 80:20), $[\alpha]_D^{27}$ = -103.2^0 (c 1, MeOH), Yield (1.6g, 63%), IR(KBr), ν_{max}/cm^{-1} 1028,1076,1172,1259,1301,1383,1450, 1506, 1602, 3198. ^{1}H NMR ($CDCl_3$ 300MHz) δ = 8.35 (s, 1H), 7.77 (d, 2H, J = 8.84Hz), 7.28-7.47 (m, 5H), 6.94 (d, 2H, J = 8.8Hz), 4.48 (dd, 1H, J = 4.6Hz), 3.94 (ddd, 2H, J = 4.67 and 3.5Hz), 3.87 (s, 3H), 2.05 (brs, 1H). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49; O, 12.53. Found: C, 74.97, H, 6.71, N, 5.58.

(R)-(+)-2-(4-methoxybenzylideneamino)-3-phenylpropan-1-ol (**3b)**

Fine needles, mp 76-77^{0}C (Pet ether: ethyl acetate, 80:20). $[\alpha]_D^{27}$= 423.56^0(c 1, MeOH), Yield (2g,72%), IR(KBr), ν_{max}/cm^{-1} 1043,1085,1080,1225,1307,1450,1512,1604,1641, 3211. ^{1}H NMR ($CDCl_3$ 300MHz) δ = 7.86 (s,1H), 7.63(d, 2H, J = 8.54Hz), 7.14-7.26(m 5H), 6.90 (d, 2H, J = 8.54Hz), 3.84 (s, 3H), 3.79-3.89(m, 2H), 3.50 (m, 1H), 2.91 (dd, 2H, J = 8.25 and 5.5Hz), 2.07(brs, 1H). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20; O, 11.88. Found: C, 75.55, H, 7.12, N, 5.26.

(R)-(+)-2-(4-methylbenzylideneamino)-2-phenylethanol **(4b)**

Pale yellow prisms, mp 80-82^{0}C (Pet ether: ethyl acetate, 80:20). $[\alpha]_D^{27}$= 84.54^0(c 1, MeOH) Yield (1.64g, 69%), IR(KBr), ν_{max}/cm^{-1} 1062, 1207, 1325, 1375, 1421, 1471, 1620(b), 3280. ^{1}HNMR ($CDCl_3$, 300MHz) δ = 8.34(s, 1H), 7.66(d, 2H J = 7.97Hz), 7.21(d, 2H J = 7.97Hz), 7.25-7.41(m, 5H), 4.47(dd, 1H J = 4.40Hz), 3.96(m, 2H), 2.36(s, 3H), 2.25(brs, 1H). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85; O, 6.69; Found: C, 80.27, H, 7.18, N, 6.04.

(S)-(-)-2-(4-methylbenzylideneamino)-2-phenylethanol **(5b)**

Yellow brown prisms, mp 80-81^{0}C (Pet ether: ethyl acetate, 80:20). $[\alpha]_D^{27}$= -107.84^0(c 1, MeOH), Yield (1.38g, 58%). IR (KBr), ν_{max}/cm^{-1} 1049, 1178, 1222, 1307, 1342, 1450, 1498, 1610, 1641, 3279. ^{1}H NMR ($CDCl_3$, 300MHz) δ = 8.35(s, 1H), 7.68(d, 2H, J = 7.93Hz), 7.21(d, 2H J = 7.93Hz), 7.26-7.44(m, 5H), 4.48(dd, 1H, J = 4.27Hz), 3.85-3.95(m, 2H), 2.39(s, 3H), 2.36(brs, 1H). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85; O, 6.69; Found: C, 80.16, H, 7.17, N, 5.99

(R)-(+)-2-(4-methylbenzylideneamino)-3-phenylpropan-1-ol (**6b)**

Colourless needles, mp 91^{0}C (Pet ether: ethyl acetate, 80:20). $[\alpha]_D^{27}$= 319.20^0 (c 1, MeOH) Yield (2.17g, 86%). IR(KBr), ν_{max}/cm^{-1} 1057(s), 1205, 1271, 1402, 1475, 1602, 3227(br). ^{1}H NMR ($CDCl_3$, 300MHz) δ = 7.95(s, 1H), 7.53(d, 2H, J = 7.93Hz), 7.12-7.35(m, 7H), 3.5(dd, 2H, J = 6.71Hz), 3.48(dd, 1H J = 6,71Hz), 2.95(ddd, 2H, J = 7.90 and 5.40Hz), 2.37(s, 3H), 2.35(brs, 1H). Anal. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53; O, 6.32. Found: C, 79.86, H, 7.41, N, 5.55

(R)-(+)-2-((2-hydroxy-1-phenylethylimino)methyl)phenol **(1c)**

Pale yellow floppy mass, mp 86-88^{0}C (Pet ether: ethyl acetate, 80:20), (87-88) [18]. $[\alpha]_D^{27}$= 160.50^0(c 1, MeOH), (99.3)[18]. Yield (2.15g, 89%). IR(KBr), ν_{max}/cm^{-1} 1024, 1045, 1087, 1174, 1261, 1305, 1448, 1512, 1604, 1637(s), 3198 (br).^{1}H NMR ($CDCl_3$, 300MHz) δ = 8.47(s, 1H), 7.25-7.40(m, 7H), 6.99(d, 1H, J = 7.15Hz), 6.87(t, 1H, J = 6.60Hz), 4.47(t, 1H, J = 6.52Hz), 3.91(d, 2H, J = 6.25Hz), 1.88(brs, 2H). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81, O, 13.26. Found: C, 74.57, H, 6.26. N, 5.72,

(S)-(-)-2-((2-hydroxy-1-phenylethylimino)methyl)phenol **(2c)**

Pale yellow spongy mass, mp 88-90^{0}C (Pet ether: ethyl acetate, 80:20), (91-93[42]. $[\alpha]_D^{27}$= -123.70^0(c 1, MeOH), (-122)[41]. Yield (1.95g, 81%), IR(KBr), ν_{max}/cm^{-1} 1024, 1045, 1087, 1174, 1261, 1305, 1448, 1512, 1604, 1637(s), 3198 (br).^{1}HNMR ($CDCl_3$, 300MHz) 8.49(s, 1H), 7.25-7.41(m,7H), 6.98(d, 1H, J = 8.25Hz), 6.89(t, 1H, J = 7.2Hz), 4.48(t, 1H, J = 6.32Hz), 3.93(d, 2H, J = 6.6Hz), 1.8(brs, 2H). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81, O, 13.26. Found: C, 74.34, H, 6.23. N, 5.85.

(S)-(+)-2-((1-hydroxy-3-phenylpropan-2-limino)methyl)phenol **(3c)**

Lemon yellow coloured crystals, mp 65^{0}C. (Pet ether: ethyl acetate, 80:20), (62-64) [43], $[\alpha]_D^{27}$= 395.04^0 (c 1, MeOH). Yield (2.37g 93%), IR(KBr), ν_{max}/cm^{-1} 1047, 1062, 1207, 1292, 1406, 1483, 1627, 3173, 3352 (br). ^{1}H NMR ($CDCl_3$) δ = 13.19(brs, 1H), 8.09(s, 1H), 7.13-7.33(m, 7H), 6.96(d, 1H, J = 8.54Hz), 6.84(t,1H J = 7.32Hz), 3.80-3.86(m, 2H), 3.48-3.36(m, 1H), 3.92,(dd,J = 8.54 and 4.88Hz). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.51, O, 12.53. Found: C, 74.83, H, 6.69. N, 5.54.

(S)-(-)-2-((1-hydroxy-3-methylbutan-2-ylimino)methyl)phenol (**4c)**

Lemon yellow spongy mass, mp 100^{0}C (Pet ether: ethyl acetate, 80:20), (104-106)[15]. $[\alpha]_D^{27}$= -29.85^0(c 0.5, MeOH) (lit.^{15}, -25), Yield (1.92g, 92%), IR 1047, 1062, 1207, 292, 1406, 1483, 1627, 3173, 3352 (br)cm^{-1}. ^{1}H NMR($CDCl_3$) δ = 8.35 (s, 1H), 7.2(dd, 2H, J = 1.65Hz), 6.90(dd, 2H, J = 7.7 and 8.25Hz), 3.79(ddd, 2H, J = 8.25 and 7.7Hz), 3.06,(q, 1H, J = 3.5,Hz), 1.94(s, 1H, J = 6.8Hz), 0.93(q, 6H, J = 6.8 and 4.1Hz). Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76; O, 15.44. Found: C, 69.57, H, 8.29. N, 6.90.

(R)-(+)-3-((2-hydroxy-1-phenylethylimino)methyl)naphthalen-2-ol (**5c)**

Greenish yellow prisms, mp 168-170^{o}C (Pet ether: ethyl acetate, 80:40), $[\alpha]_D^{27}$ = 198.76^{o}(c 0.5, MeOH), Yield (1.97g, 68%), IR(KBr), ν_{max}/cm^{-1} 1078,1174,1276,1406(w), 1489, 1541,1630(s),3230(brs), ^{1}H NMR ($CDCl_3$, 300MHz) δ = 14.96(brs, 1H), 8.9(s, 1H), 7.81(d, 1H, J = 8.54Hz),7.16-7.53(m, 9H), 6.88(d, 1H, J = 9.76Hz), 4.68(dd, 1H, J = 4.67Hz), 3.99-4.06(m, 2H), 3.5(brs, 1H). Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81; O, 10.98. Found: C, 77.84, H, 5.67: N, 4.63.

(S)-(-)-3-((2-hydroxy-1-phenylethylimino)methyl)naphthalen-2-ol **(6c)**

Yellow floppy mass, mp 165-166^{o}C (Pet ether: ethyl acetate, 80:40), $[\alpha]_D^{27}$ = -202.08^{o}(c 0.5, MeOH) Yield (1.94g, 67%,) IR(KBr),ν_{max}/cm^{-1}1078,1174,1276,1406(w),1489, 541,1630(s),
3230. ^{1}H NMR ($CDCl_3$, 300MHz) δ = 14.96(brs, 1H), 902(s, 1H), 7.88(d, 1H, J =8.43Hz), 7.63(d,1H, J = 9.28Hz), 7.57(d, 1H, J = 8.15Hz), 7.23-7.46(m, 7H), 6.96(d, 1H, J = 8.99Hz), 4.68(dd, 1H, J = 5.3Hz), 4.0(t, 2H, J = 4.5Hz), 2.93(brs, 1H). Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81; O, 10.98. Found: C, 77.79, H, 5.87: N, 4.92.

(S)-(+)-3-((1-hydroxy-3-phenylpropan-2-ylimino)methyl) naphthalen-2-ol **(7c)**

Brown yellow floppy mass, mp 170-171^{o}C (Pet ether: ethyl acetate, 80:40), $[\alpha]_D^{27}$ = 467.80^{o}(c 1, MeOH), Yield (2.13g, 70%), IR(KBr), ν_{max}/cm^{-1} 1047, 1062, 1207, 1292, 1406, 1483, 1627, 3173, 3352 (br). ^{1}H NMR ($CDCl_3$, 300MHz) δ = 14.95(brs, 1H), 8.49(s, 1H), 7.58(d, 1H, J = 8.53Hz), 7.12-7.48(m, 9H), 7.80(d, 1H, J =9.35Hz), 3.91(dd, 1H, J = 8.52Hz), 3.50(brs 1H), 3.01(ddd, 2H, J = 7.79 and 4.95Hz). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59; O, 10.48. Found: C, 78.50, H, 6.26: N, 4.59.

(S)-(-)-3-((1-hydroxy-3-methylbutan-2-ylimino)methyl)naphthalen-2-ol (**8c)**

Yellow floppy mass, mp 92-95^{o}C (Pet ether: ethyl acetate, 80:40), $[\alpha]_D^{27}$ = -60.26^{o}(c 0.6, MeOH), Yield (1.79g, 70%), IR(KBr), ν_{max}/cm^{-1} 1047, 1062, 1207, 1292, 1406, 1483, 1632, 3173, 3342 (br). ^{1}H NMR ($CDCl_3$, 300MHz) δ = 14.29(brs, 1H),8.65(s, 1H), 7.57(d, 1H, J = 8.54Hz), 7.11-7.46(m, 4H), 6.77(d, 1H, J = 8.54Hz),4.50(brs, 1H), 3.79(ddd, 2H, J = 8.8 and 3.9Hz), 3.29(d, 1H, J = 3.8Hz), 0.83(dd, 6H, J = 7.7Hz). Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44; O, 12.44. Found: C, 74.50, H, 7.36: N, 5.42.

***General procedure for synthesis of dialdehydes* 9-12**

Dialdehydes **9-12** were synthesized according to known procedure [30]

2,2'-(ethane-1,2-diylbis(oxy))dibenzaldehyde **9**

Colourless, mp 127^{0}C(Ethanol), Yield (5.13g, 38%), IR(KBr), ν_{max}/cm^{-1} 1064,1107, 1247, 1294, 1400, 1452, 1485, 1597, 1685,2771(s),3338. ^{1}H NMR ($CDCl_3$, 300MHz) δ = 10.44 (s, 2H), 7.05-7.86(m, 8H), 4.53δ (s, 4H).

4,4'-(ethane-1,2-diylbis(oxy))dibenzaldehyde **10**

Colourless,mp 115^{0}C (Ethanol), Yield (6.35g, 47 %,), IR(KBr), ν_{max}/cm^{-1} 1072, 1112, 1226,1259, 1427, 1460, 1508,1599, 1687, 2758(s), 2850, 2945, 3064, 3350. 1H NMR ($CDCl_3$, 300MHz) δ = 9.89(s, 2H), 7.85(d, 4H, J = 8.8Hz), 7.05 (d, 4H, J=8.5Hz), 4.44δ (s, 4H).

2,2'-(butane-1,4-diylbis(oxy))dibenzaldehyde **11**

Coloursless, mp 110 ^{0}C (Ethanol), Yield (6.5g, 44%), IR (KBr), ν_{max}/cm^{-1} 1045, 1109, 1244, 1305, 1510, 1600, 1681(s), 2843, 2953, 3039(w). ^{1}H NMR δ = 10.95(s, 2H), 7.83, (dd, 2H, J = 1.65Hz), 7.51-7.57(m, 2H), 6.97-7.06(m, 8H), 4.19δ, (s, 4H), 2.10(s, 4H).

4,4'-(butane-1,4-diylbis(oxy))dibenzaldehyde **12**

Brown flakes, mp 100^{0}C(Ethanol), Yield (6.94g, 47%), IR (KBr), ν_{max}/cm^{-1} 1045, 1109, 1244, 1305, 1510, 1600, 1681(s), 2843, 2953, 3039(w). ^{1}H NMR($CDCl_3$, 300MHz) δ = 9.89, (s, 2H), 7.84(d, 4H, J = 8.5Hz), 7.14, (d, 4H, J = 8.5Hz), 4.14(s, 4H), 2.05δ, (s, 4H).

General procedure for synthesis of diimines **1d-4d** ***and*** **1e-6e**

In a round bottom flask equipped with Teflon coated magnetic bar with a magnetic stirrer and a reflux condenser were introduced 1mmol of dialdehydes and 25 ml distilled water. The β-amino alcohol (2 mmol) was added in one portion and the flask was kept at room temperature under vigorous mechanical stirring for 30 minutes. The flask was transferred to oil bath and stirring continued for 16-24h with oil bath temperature 110 ^{o}C. Reaction progress was checked by TLC. The flask was allowed to cool, after completion of the reaction, if no precipitation occurred, the aqueous reaction mixture was extracted thrice with diethyl ether. The combined organic layers were dried over Na_2SO_4. The organic solvent was evaporated off and the residue was analyzed by GC and NMR. All the synthesized diimines are solid substances and are purified by recrystallization from hot pet ether and ethyl acetate (1:1).

The data for diimines

(2R,2'R)-(+)-(2,2'-(ethane-1,2-diylbis(oxy))bis(2,1-phenylene))
bis(methan-1-yl-1-ylidene)bis(azan-1-yl-1-ylidene))

bis(2-phenylethanol) (**1d)**

Colourless amorphous solid, mp 88-90 ^{0}C (Pet ether: ethyl acetate, 1:1), Yield (0.24g, 47%), $[\alpha]_D^{27}$ = 102^o (c .05, $CHCl_2$). IR(KBr),ν_{max}/cm^{-1}1055,1114,1161,1238,1290, 1384,1452,1485, 1597,1633(s),2874,2922, 3066, 3171(br), 3441. ^{1}H NMR ($CDCl_3$, 300MHz) δ = 8.72(s,2H), 8.10(d, 2H, J = 1.79Hz), 7.20-7.43(m, 12H), 7.04(t, 2H, J = 7.6Hz), 6.96(d, 2H, J = 8.50Hz), 4.39(s, 4H), 4.32(dd, 2H, J = 4.5Hz), 3.74-3.91(m, 4H), 2.45(brs, 2H). Anal. Calcd for $C_{32}H_{32}N_2O_4$: C, 75.57; H, 6.34; N, 5.51; O, 12.58. Found: C, 75.34, H, 6.54. N, 5.23.

(2S,2'S)-(-)-(2,2'-(ethane-1,2-diylbis(oxy))bis(2,1-phenylene))bis(methan-1-yl-1-ylidene)bis(azan-1-yl-1 ylidene))bis(2-phenylethanol) (**2d)**

Colourless amorphous solid, mp 65 ^{0}C (Pet ether: ethyl acetate, 1:1), (0.27g, 54%),$[\alpha]_D^{27}$ =-248^o (c 0.05, CH_2Cl_2). IR(KBr) 1055, 1114,1161,1238,1290,1384, 1452,1485,1597,1633(s), 2874,2922,3066,3171(br),3441cm^{-1}.^{1}HNMR ($CDCl_3$, 300MHz) δ = 8.74 (s, 2H), 8.10(d, 2H, J = 1.8Hz), 6.89-7.55(m, 14H), 4.40(s, 4H), 4.34(s, 2H), 3.84-3.93(m, 2H), 3.78(s, 4H), 2.18(brs, 2H). Anal. Calcd for $C_{32}H_{32}N_2O_4$: C, 75.57; H, 6.34; N, 5.51; O, 12.58. Found: C, 75.10, H, 6.19, N, 5.40.

(2R,2'R)-(+)-(2,2'-(ethane-1,2-diylbis(oxy))bis(2,1-phenylene))bis(methan-1-yl-1-ylidene)bis(azan-1-yl-1-ylidene))bis(3-phenylpropan-1-ol) **(3d)**

Colourless solid, mp 100 ^{0}C (Pet ether: ethyl acetate, 1:1), (0.34g, 64%),$[\alpha]_D^{27}$ = 400^o (c 0.05, CH_2Cl_2). IR(KBr), ν_{max}/cm^{-1} 1055,1114,1161,1238,1290,1384,1452,1485,1597,1633(s), 2874, 2922,3066,3171(br), 3441. ^{1}H NMR ($CDCl_3$, 300MHz) δ = 7.89(s, 2H), 7.58(d, 4H, J = 8.30Hz), 7.12-7.37(m, 10H), 6.93(d, 4H, J = 7.79Hz), 4.35(s, 4H), 3.78(ddd, 4H, J = 2.5, 3,4 and 6.8Hz), 3.35(brs, 2H), 2.9(dddd,4H, J = 4.9, 5.3,83Hz), 2.3(brs, 2H). Anal. Calcd for $C_{34}H_{36}N_2O_4$: C, 76.09; H, 6.76; N, 5.22; O, 11.93. Found: C, 75.86, H, 6.92. N, 5.09.

(2R,2'R)-(+)-(2,2'-(butane-1,4-diylbis(oxy))bis(2,1-phenylene))bis(methan-1-yl-1-ylidene)bis(azan-1-yl-1-ylidene))bis(3-phenylpropan-1-ol) **(4d)**

Colourless, mp 168-170 ^{0}C (Pet ether: ethyl acetate, 1:1), yield (0.36g, 68%), $[\alpha]_D^{27}$ = 315.08^o (c 0.5, CH_2Cl_2). IR(KBr), ν_{max}/cm^{-1} 1058,1116, 1161, 1228,1290,1384, 1452,1485,1597, 1633(s), 2874, 2922,3066,3171(br), 3445. ^{1}H NMR ($CDCl_3$, 300MHz) δ = 8.42(s, 2H), 7.88(dd, 2H, J = 1.7Hz), 6.94-7.32(m,

14H), 6.84(dd, 4H, J = 1.7Hz), 4.12(s, 4H), 3.7(brs, 2H), 3.37(s. 4H), 2.92(dddd, 4H, J = 5.3, 6.8Hz), 2.45(brs, 2H), 2.04(s, 4H). Anal. Calcd for $C_{34}H_{36}N_2O_4$: C, 76.09; H, 6.76; N, 5.22; O, 11.93. Found: C, 75.66, H, 6.62. N, 5.14

(2R,2'R)-(+)2,2'-(((ethane-1,2-diylbis(oxy))bis(4,1-phenylene))bis(methanylylidene))bis(azanylylidene))bis(2-phenylethanol) (**1e**)

Colourless, mp 142-144 ^{0}C (Pet ether: ethyl acetate, 1:1), Yield (0.29g, 57%), $[\alpha]_D^{29.6}$ = 184.4^o(c 0.1 CH_2Cl_2). IR(KBr), ν_{max}/cm^{-1} 1035,1070, 1174,1247,1506,1600, 1633(s), 2868, 2928, 3242(br)cm^{-1} ^{1}H NMR ($CDCl_3$,300MHz) δ = 8.35(s, 2H), 7.77(d, 4H, J = 8,6Hz), 7.28-7.46 (m, 10H), 6.99(d, 4H, J = 8,6Hz), 4.48(dd, 2H J = 4.8Hz), 4.40(s, 4H), 3.94(dd, 4H, J = 4.8Hz), 2.06(brs, 2H). Anal. Calcd for $C_{32}H_{32}N_2O_4$: C, 75.57; H, 6.34; N, 5.51; O, 12.58; Found: C, 74.76; H, 6.36; N, 5.43.

(2S,2'S)-(-)-2,2'-(((ethane-1,2-diylbis(oxy))bis(4,1-phenylene))bis(methanylylidene))bis(azanylylidene))bis(2-phenylethanol) (**2e**)

Colourless, mp 144-146 ^{0}C (Pet ether: ethyl acetate, 1:1), Yield (0.3g, 57%), $[\alpha]_D^{29.3}$ = -120^o(c 0.1 CH_2Cl_2). IR(KBr), ν_{max}/cm^{-1} 1035,1070, 1174,1247,1506,1600, 1633(s), 2866, 2928, 3242(br). ^{1}H NMR ($CDCl_3$, 300MHz) δ = 8.36(s, 2H), 7.78(d, 4H, J = 9Hz), 7.28-7.47 (m, 10H), 6.99(d, 4H, J = 9Hz), 4.47(dd, 2H J = 4.8Hz), 4.40(s, 4H), 3.94(dd, 4H, J = 4.8Hz), 2.06(brs, 2H). Calcd for $C_{32}H_{32}N_2O_4$: C, 75.57; H, 6.34; N, 5.51; O, 12.58; Found: C, 74.70; H, 6.33; N, 5.38.

(2R,2'R)-(+)-2,2'-(((ethane-1,2-diylbis(oxy))bis(4,1-phenylene))bis(methanylylidene))bis(azanylylidene))bis(3-phenylpropan-1-ol) (**3e**)

Colourless, mp 116-118 ^{0}C (Pet ether: ethyl acetate, 1:1), Yield (0.35g, 67%), $[\alpha]_D^{29.5}$ = 166.4^o(c 0.1 CH_2Cl_2). IR(KBr), ν_{max}/cm^{-1} 1043,1074, 1170,1244,1575,1604, 1635(s), 2858, 2928, 3433br). ^{1}H NMR ($CDCl_3$,300MHz) δ = 7.92(s, 2H), 7.61(d, 4H, J = 9Hz), 7.24-7.27 (m, 10H), 6.95(d, 4H, J = 9Hz), 4.36(s, 4H), 4.40(s, 4H), 3.89(dd, 4H, J = 3.4Hz), 3.40(m, 2H), 2.90(dd, 4H, J = 8.1 and 5.8Hz), 2.0(brs, 2H). Calcd for $C_{34}H_{36}N_2O_4$: C, 76.09; H, 6.76; N, 5.22; O, 11.93; Found: C, 75.96; H, 6.60; N, 5.13.

(2R,2'R)-(+)-(4,4'-(butane-1,4-diylbis(oxy))bis(4,1-phenylene))bis(methan-1-yl-1-ylidene)bis(azan-1-yl-1-ylidene))bis(2-phenylethanol) (**4e**)

Colourless, mp 100 ^{0}C (Pet ether: ethyl acetate, 1:1), Yield (0.33g, 63%), $[\alpha]_D^{29.7}$ = 331.80^o(c 0.1 CH_2Cl_2). IR(KBr), ν_{max}/cm^{-1} 1041,1064, 1172,1251,1508,1602, 1635(s), 2868, 2924, 3234(brs)cm^{-1} ^{1}H NMR ($CDCl_3$,300MHz) δ = 8.33(s, 2H), 7.74(d, 4H, J = 8.5Hz), 7.27-7.45 (m, 10H), 6.92(d, 4H, J = 8.5Hz), 4.46(dd, 2H, J = 4.3Hz), 4.08(s, 4H), 3.92(dd, 4H, J = 4.3Hz), 2.0(s, 4H), 1.79(brs, 2H). Calcd for $C_{34}H_{36}N_2O_4$: C, 76.09; H, 6.76; N, 5.22; O, 11.93; Found: C, 74.79; H, 6.80; N, 5.50.

(2S,2'S)-2,2'(-)-(4,4'-(butane-1,4-diylbis(oxy))bis(4,1-phenylene))bis(methan-1-yl-1-ylidene)bis(azan-1-yl-1-ylidene))bis(2-phenylethanol) (**5e**)

Colourless, mp 98 ^{0}C (Pet ether: ethyl acetate, 1:1), Yield (0.37g, 70%), $[\alpha]_D^{29.3}$ = -71.6^o(c 0.1 CH_2Cl_2). IR(KBr), ν_{max}/cm^{-1} 1049, 1170,1247,1508,1602, 1637(s), 2872, 2943, 3377(br). ^{1}H NMR ($CDCl_3$,300MHz) δ = 8.32(s, 2H), 7.72(d, 4H, J = 8.5Hz), 7.26-7.48 (m, 10H), 6.92(d, 4H, J = 8.5Hz), 4.46(dd, 2H, J = 4.8Hz), 4.06(s, 4H), 3.91(dd, 4H, J = 4.8Hz), 2.06(brs, 2H), 2.0(s, 4H). Calcd for $C_{34}H_{36}N_2O_4$: C, 76.09; H, 6.76; N, 5.22; O, 11.93; Found: C, 75.17; H, 6.50; N, 5.30.

(2R,2'R)-(+)-(4,4'-(butane-1,4-diylbis(oxy))bis(4,1-phenylene))bis(methan-1-yl-1-ylidene)bis(azan-1-yl-1-ylidene))bis(3-phenylpropan-1-ol) (**6e**)

Colourless, mp 86 ^{0}C (Pet ether: ethyl acetate, 1:1), Yield (0.40g, 72%), $[\alpha]_D^{29.5}$ = 189.4^o(c 0.1 CH_2Cl_2). IR(KBr), ν_{max}/cm^{-1} 1047,1082, 1172,1251,1510,1602, 1637(s), 2862, 2920, 3227(br). ^{1}H NMR ($CDCl_3$,300MHz) δ = 7.91(s, 2H), 7.58(d, 4H, J = 9Hz), 7.13-7.31 (m, 10H), 6.88(d, 4H, J = 9Hz), 4.06(s, 4H), 3.77(dd, 4H, J = 3.8Hz), 3.48(brs, 2H), 2..91(dddd, 4H, J = 8.1 and 5.3Hz), 2.03(brs, 2H), 1.98(s, 4H). Calcd for $C_{36}H_{40}N_2O_4$: C, 76.57; H, 7.14; N, 4.96; O, 11.33; Found: C, 75.28; H, 7.24; N, 5.05.

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RESULTS AND DISCUSSION

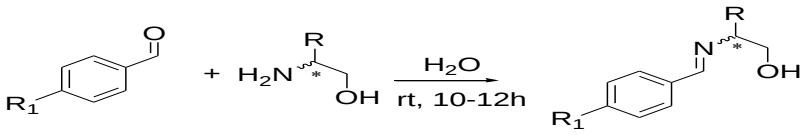
Synthesis of monoimines

Schiff bases of aromatic aldehydes are usually easy to obtain under mild conditions at relatively low temperature, by condensation reaction with amines [31]. General chemistry of this process showed a two-step reaction, with intermediate formation of amino alcohol and final elimination of water [32]. Thus, in order to obtain desired product excess of suitable organic solvent is generally used for azeotropic removal of water from the system [15, 16]. In a completely different approach, we attempted the synthesis of variety of chiral imine derivatives in water and in the absence of any catalyst or buffering mixture. As a starting material in the first series, p-methoxy and p-methyl benzaldehydes (5 and 6) together with chiral β-amino alcohols (1a- 4a) were used to get chiral monoimines 1b-6b (Scheme-1). β-Amino alcohols are readily soluble in water, on the other hand aromatic aldehydes form emulsion droplets in water at room temperature. These droplets generally contain hydrophobic interiors which would concentrate the β-amino alcohols onto the surface of droplets and enhance the reaction rate towards the side of dehydrated product. Water molecules generated during the reaction are expelled out from droplets due to hydrophobic nature of their interiors which shifts the equilibrium towards the product. Mono imines of this series are isolated by extraction of aqueous reaction mixture with diethyl ether. The crude products, after characterization by IR, NMR and GC showed a trace amount of unreacted aldehydes. Recrystallization of the crude product from hot pet ether eliminated the aldehyde impurity and yielded solid monoimines of high purity. Same process is being used for all the monoamines of this series (Table-1).

Table 1: Condensation of o-and p-substituted benzaldehyde with β-amino alcohols to obtain bi-dentate and tri-dentate CSBLs.

Sr. No	Compound	Time (h)	Yield (%)	mp (^{o}C)	$[\alpha]_D^{27}$
1	**1b**	12	66	85	98.72
2	**2b**	12	63	94-95	-103.20
3	**3b**	18	74	76-77	423.56
4	**4b**	12	69	80-82	84.54
5	**5b**	12	58	80-81	-107.84
6	**6b**	10	86	91	319.20
7	**1c**	02	89	86-88 (87-88)[18]	160.50 (99.3)[18]
8	**2c**	02	81	88-90 (91-93)[42]	-123.70 (-122)[41]
9	**3c**	02	93	65 (62-64)[43]	395.04
10	**4c**	04	92	100 (104-106) [15]	-29.85 (-25)[15]
11	**5c**	06	68	168-170	198.76
12	**6c**	06	67	165-166	-202.08
13	**7c**	06	70	170-171	467.80
14	**8c**	06	70	92-95	-60.26

Note: Literature values of mp and $[\alpha]_D^{oC}$ are given in the brackets



5, R_1 = OMe
6, R_1 = Me

1b. (R)-(+)-R = Ph, $R_1 = OCH_3$
2b. (S)-(-)-R = Ph, $R_1 = OCH_3$
3b. (R)-(+)-R = CH_2Ph, $R_1 = OCH_3$
4b. (R)-(+)-R = Ph, $R_1 = CH_3$
5b. (S)-(-)-R = Ph, $R_1 = CH_3$
6b. (R)-(+)-R = CH_2Ph, $R_1 = CH_3$

Scheme 1: Condensation of β- amino alcohols with 4-methoxybenzaldehyde and 4-methylbenzaldehyde in water

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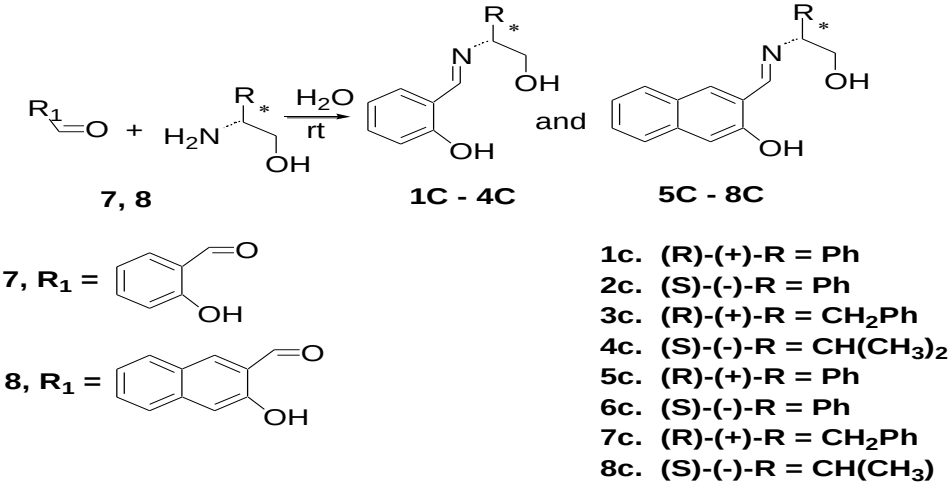
Similarly in another attempt, *o*-hydroxy aromatic aldehydes (7, 8) are condensed with same β-amino alcohols (1a-4a) in water (Scheme -2). The condensation reaction occurred within mixing time at room temperature and solid monoimines separated as a precipitate in quantitative yields (Table-1). The monoimines thus obtained are purified by recrystallization from hot pet ether. The spectroscopic analysis showed highest purity for these monoimines except for compounds 5c-8c, in which little amount of unreacted adehyde remained along with the product. The compounds 7c and 8c required purification by column chromatography.
To verify the role of organic solvents in monoimines synthesis the condensation reaction was carried out in different solvents *viz*. absolute ethanol, methanol, DMF and CH_3CN at room temperature and then at elevated temperatures. In case of salicyldimine (1c) the reaction mixture in absolute ethanol was refluxed for 16 hours. Analysis of product by GC showed almost 40% starting aldehyde in the reaction mixture. Similar results are furnished in other solvents and condensation reaction failed to obtain the solid imines. Thus use of organic solvents for synthesis of monoimines did not seem to be more effective than water. Although the compounds 1b-6b required organic solvents for extraction at the work up stage, remaining monoimines are synthesized completely in aqueous solution. These chiral imines can be directly used to synthesize metal complexes since, the unreacted aldehydes if present may not act as good ligands. After successful result in monoimines synthesis, our attention was diverted towards the synthesis of chiral diimines which could be used as possible chelating agents for variety of metal cations.



Scheme 2: Condensation of β - amino alcohols with 2-hydroxybenzaldehyde and 3-hydroxynaphthalene-2-carbaldehyde in water

Synthesis of open chain diimines

Most of the diimines are synthesized from alkyl diamines and suitable aldehydes/ ketones to constitute Schiff bases which could be transformed into metal ion salen complexes as successful chiral catalysts [33, 34]. The synthesis of such salen complexes in the present report is restricted, since we used optically pure β-amino alcohols (1a-4a) as a primary source of chirality.

Aromatic dialdehydes (11-14) were obtained by bridging *p*-hydroxy and *o*-hydroxy benzaldehydes with dibromoalkanes (n = 2, 4) in 2% NaOH by known procedure [34]. The synthesis of diimine was designed by similar condensation of dialdehydes wth chiral β-amino alcohols in water at room temperature (Scheme - 3). The diimines formed may be used as possible chelating agents to coordinate with metal ion through N and O mixed donor atoms.

Initially, stoichiometric quantities of dialdehydes and β-amino alcohols (little exess) were stirred in water at room temperature. The progress of reaction was monitored by extracting aqueous reaction mixture after every two hours by TLC, GC, IR and NMR techniques. The analysis of reaction mixture revealed partial diimine formation. Therefore, stirring was continued for prolonged time at the same temperature. Even after prolonged time, reaction could not go to completion. The GC analysis of crude product indicated monoimine formation instead of diimine which was further confirmed by IR and NMR spectroscopic analysis. Aldehyde carbonyl (>C=O) and imine (>C=N-) group frequencies appear very close to each other (1710-1785 and 1689-

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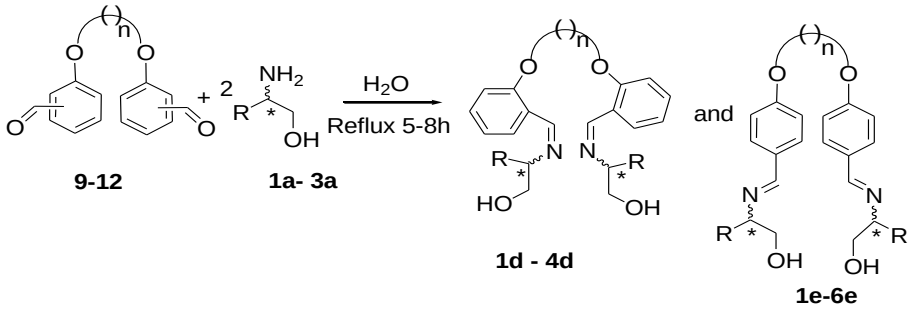
1471 cm^{-1} respectively). Two distinct peaks at 1688 cm^{-1} (>C=O) and 1638 cm^{-1}(>C=N-) respectively in the IR spectrum of crude product confirmed the monoimine formation since the latter frequency for imine is not present in the starting dialdehyde. Similar observations were made by examining the NMR spectra, where both peaks for aldehyde proton singlet at 9.9δ and for imine proton at 8.34δ were appeared simultaneously in the NMR spectra.



1d, (R,R)-(+)- R = Ph, n = 2
2d, (S,S)-(-)- R = Ph, n = 2
3d, (R,R)-(+)- R = CH_2Ph, n = 2
4d, (R,R)-(+)- R = Ph, n = 4

1e, (R,R)-(+)- R = Ph, n = 2
2e, (S,S)-(-)- R = Ph, n = 2
3e, (R,R)-(+)- R = CH_2Ph, n = 2
4e, (R,R)-(+)- R = Ph, n = 4
5e, (S,S)-(-)- R = Ph, n = 4
6e, (R,R)-(+)- R = CH_2Ph, n = 4

Scheme 3: Condensation of β - amino alcohols with dibenzaldehydes in water

In the initial stage of diimine synthesis, we presumed that solvent might be playing an important role; therefore the diimine synthesis was also carried out by changing the solvent such as absolute EtOH, MeOH, DMF and CH_3CN at room temperature as well as at elevated temperature. In these conditions also similar results were obtained. Finally the reaction mixture along with excess of β-amino alcohols was refluxed in distilled water for few hours in oil bath. As mentioned previously, β-amino alcohols are readily soluble in water, but dialdehydes remained insoluble at room temperature. These dialdehydes formed oil droplets at elevated temperature and reaction proceed towards the product which was separated as a white precipitate from aqueous solution (Scheme 3). The refluxing continued for 3-6 hrs. The product separated by filtration, was purified by recrystallization from hot pet ether and ethyl acetate.

NMR and IR spectroscopy confirmed diimine formation except for compound 2d and 4d where minor peak appeared in NMR spectroscopy at 9.9δ indicating aldehyde proton. The purity of all other compounds was confirmed by GC, IR, NMR and elemental analysis. The aldehyde proton peak in NMR completely disappeared and a new peak for imine proton appeared at lower chemical shift (8.34δ) than the aldehydic proton chemical shift. The IR spectrum also confirmed the absence of aldehyde carbonyl frequency and new frequency for imine (–HC=N-) bond appeared at 1633cm^{-1}. Thus a series of diimines 1d-4d and 1e-6e are synthesized by refluxing stoichiometric quantities of the suitable β-amino alcohols (slightly excess) and dialdehydes in aqueous solution in good yields (Table - 2). The specific rotation for all CSBLs synthesized is measured in $MeOH/CH_2Cl_2$ at room temperature.

Table 2: Condensation of o-and p- substituted dialdehydes with β-amino alcohols to obtain tetra dentate CSBLs.

Sr. No	Compound	Time (h)	Yield (%)	mp (°C)	$[\alpha]_D^{oC}$
1	**1d**	6	62	88-90	102.72
2	**2d**	5	54	65	-248.00
3	**3d**	8	64	100	400.20
4	4**d**	8	68	168-170	315.08
5	**1e**	6	57	142-144	184.40
6	**2e**	6	57	142-144	-120
7	**3e**	6	67	116-118	166.40
8	**4e**	6	63	100	331.80
9	**5e**	6	70	98	-71.60
10	**6e**	5	72	86	189.4

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UV-visible Spectroscopic Study

UV- visible spectra of all the CSBLs synthesized were studied for their structural differences. Dilute solutions (1.0 - 1.5 X 10^{-5}M) in MeOH / CH_2Cl_2, depending upon the solubility of CSBLs were prepared for electronic absorption spectra. Electronic spectra of Schiff bases, generally feature a strong band below 300nm and a medium band between 300-335nm with absorption maxima (λ_{max}) at 308-320nm due to intra-ligand n-Л* and Л-Л* transitions respectively [35-37]. Electronic absorption of CSBLs (**1b-6b**) in MeOH show absorption maxima at 254-269nm (ε = 11930-26090 $dm^3m^{-1}cm^{-1}$) below 300nm for azomethane (**Fig. 1**). In case of CSBLs **1b-3b** this band shifts towards longer wavelength (269nm) as expected due to *p*-methoxy in aromatic aldehyde of parent chromophore but this effect is not prominent in **4b- 6b** since in these CSBLs aromatic aldehyde moiety is substituted with *p*-methyl group.

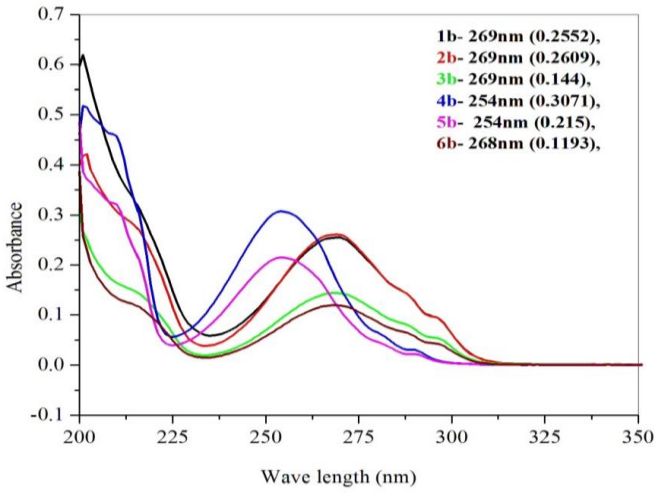

Figure 1: UV – visible spectra of 1.0-1-5 x 10^{-5}M solutions of CSBLs 1b-6b in MeOH (Values in the bracket indicate absorbance of individual λmax.)

CSBLs synthesized by condensation of salicyldehyde and 2-hydroxy naphthaldehyde with β-amino alcohols (**1c-7c**) shows further enhancement in the absorption maxima in addition to the band below 300nm. Additional bands (307-316nm, ε = 3100-4990 dm^3m^{-1} cm^{-1}) for**1c-4c** and two bands at longer wavelength (400-420nm) for **5c-7c** (**Fig. 2**) are observed. The additional band at 307-316nm is attributed to the strong intra-molecular H-bonding between *o*-hydroxyl of the aromatic aldehyde moiety and N of azomethane [38, 39] H-bonding helps to maintain the co-planarity of the overall chromophore to extend the conjugation. Well resolved two bands with appreciable intensity at 400 - 420nm appeared for **5c-7c** which are due to naphthalene ring of the aldehyde moiety [40].

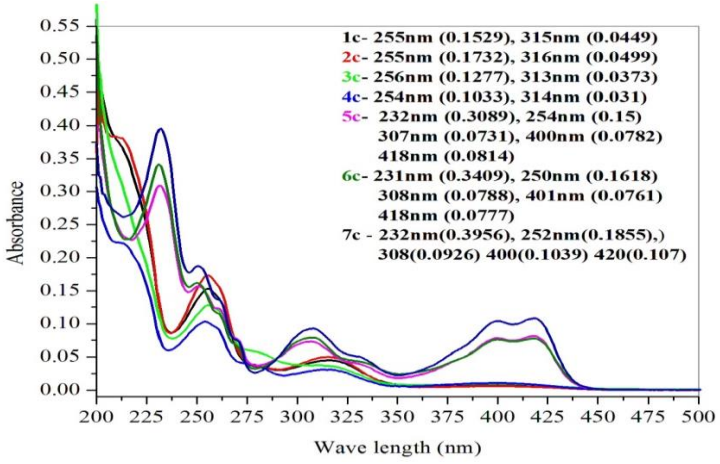

Figure 2: UV – visible spectra of 1.0 x 10^{-5}M solutions of CSBLs 1c-7c in MeOH (Values in the bracket indicate absorbance of individual λmax.)

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C_2 symmetric diimines **1d-7d** in CH_2Cl_2 exhibit a strong single band at 271-272 nm (ε = 45240-113100 dm^3m^{-1} cm^{-1}). The effect of double identical chromophore (azomethane) is not observed in the electronic spectra of these CSBLs (**Fig.3**). A small rise in the wave length as compared to first type of CSBLs (**1b-6b**) may be due to solvent effect.

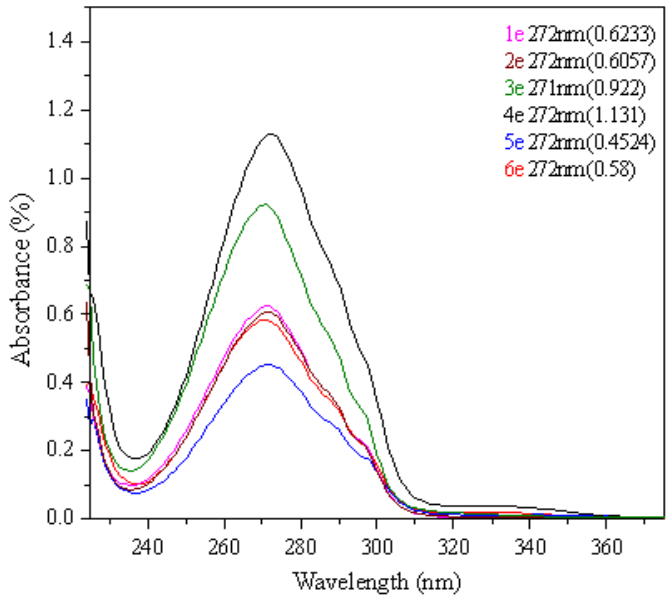

Figure 3: UV – visible spectra of 1.0 – 1.5 x 10^{-5}M solutions of CSBLs 1d-6d in CH_2Cl_2 (Values in the bracket indicate absorbance of individual λmax.)

CONCLUSIONS

Organic solvents proved to be less effective than water to obtain the chiral imines and diimines in quantative yield. A simple and convenient route is developed to synthesize CSBLs by condensation of aldehydes and dialdehydes with optically active β-amino alcohols in water without using any catalyst or buffer. Condensation of o-hydroxy aldehydes with β-amino alcohols is rapid and provide excellent yield at room temperature. The synthesis of monoimines and diimines can be achieved completely in aqueous medium in excellent yield except for monoimnes of p-methoxy/methyl substituted aldehydes where organic solvent is used for extraction of aqueous reaction mixture to isolate the CSBLs. All other monoimines and diimines are separated from aqueous medium after completion of reactions as a precipitate. Diimine synthesis requires boiling of aqueous reaction mixture. Co planarity of aromatic ring and azomethane is maintained due to strong intramolecular H-bonding in o-hydroxy imines which is responsible for longer wavelength of absorption in uv-vis. spectroscopy.

The synthesized CSBLs may be explored as bidentate or tridentate chiral ligands while diimines as a chelating agent for synthesis of chiral transition metal complexes which are generally excellent chiral catalyst for many organic transformations in organic synthesis.

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